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**Water Particulate Contamination of PET Based Bottles**

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A limited study of both defective and undamaged PET based water (Desani brand) bottles has been conducted using a combination of scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS). The internal surface of the defective bottles was known to have exfoliated small fragments of PET into the water. These fragments were confirmed to be PET in separate studies within Coca-Cola. Using SEM we were able to show that the damage to the internal surface of the bottles is most prevalent at the loci of maximum curvature relating to the contours of the bottle (see Figure 1). These areas showed a large degree of surface damage and exfoliation. The damage was not wholly restricted to the areas of maximum curvature, since damage to the other flatter areas of the internal surface were also noted, but the failure and therefore exfoliation was significantly less. Using DSC we measured the transition temperatures and melt behaviour of the exfoliated PET in addition to a section of PET from an undamaged PET bottle. The section of the latter sample was through the entire thickness of the bottle wall and therefore includes the internal surface. However, since the thickness of the exfoliated layers of PET were only a few microns, these only represent a small percentage of the total PET and therefore DSC data from the undamaged PET is dominated by the majority PET wall thickness and not the surface. The DSC measurements show that the exfoliated material is slightly more crystalline (based on area of melt peak) than the bulk of the PET (37.2J/g compared to 32.4 J/g, respectively). It should be noted that these data were only obtained from a single sample so the significance of this difference may not be statistical and requires repeated runs to confirm.

Careful measurements of chemical composition have been undertaken using XPS. This technique is sensitive to atomic species (except hydrogen) and allows quantitative determination of atomic ratios of the near surface region of the sample to be established. The technique probes the sample surface using a X-ray beam collimated to approximately 500-800 μm diameter, from the stimulated photoemission the atomic species present as well which orbital it came from can easily be determined. The internal surface of an undamaged bottle was compared to the surface exposed by exfoliation. It is not possible to determine the surface properties of the PET particulates. Since the technique can not detect H, the only species detected from both samples were C, O and N. C and O are of course expected from PET but the N must be associated with additives to the bottle formulation. The theoretical atomic ratio for PET for C:O:N is 10:4:0 or a % ration of 71.4:28.6:0. From the peak areas of the 1s electron orbitals of all three atomic species the atomic ratio of these elements were evaluated. The surface of the standard bottle gave a C:O:N % ratio (averaged over two samples) of 76.5:20.8:2.7. Clearly N is present from one or more additives that are present at the surface. By comparison, the C:O:N % ratio (averaged over two samples) for the exfoliated surface is 69.5:26.8:3.6. Quite clearly the surfaces of the outer and exfoliated materials are chemically different, and it should also be noted that they are both different from the values expected from PET. This is perhaps not surprising since it is known that the surface of polymer blends is often different from the bulk. In this case the blend results from the inclusion of one of two possible additives which possess C:O:N ratios of 7:1:2 and 9:1:2. However, even accounting for the presence of either one of these additives it is not possible to explain either of the two experimentally determined surface compositions. Further work on these samples are to be conducted, but the XPS facility has been under repair and measurements will resume when these are complete.

In summary, although the measurements are not complete, the evidence so far obtained indicates that the curvature of the bottle has made stress concentrations. The variation in composition between the surface and sub-surface PET is thought to create a weak point which is compounded with the stress concentration to create fracturing parallel to the surface and therefore exfoliation of PET fragments. However, without further measurements both to resolve the outstanding issues as well as chemical depth sensitive measurements this summary remains untested.

Figure 1. SEM images of internal surface of faulty bottles.

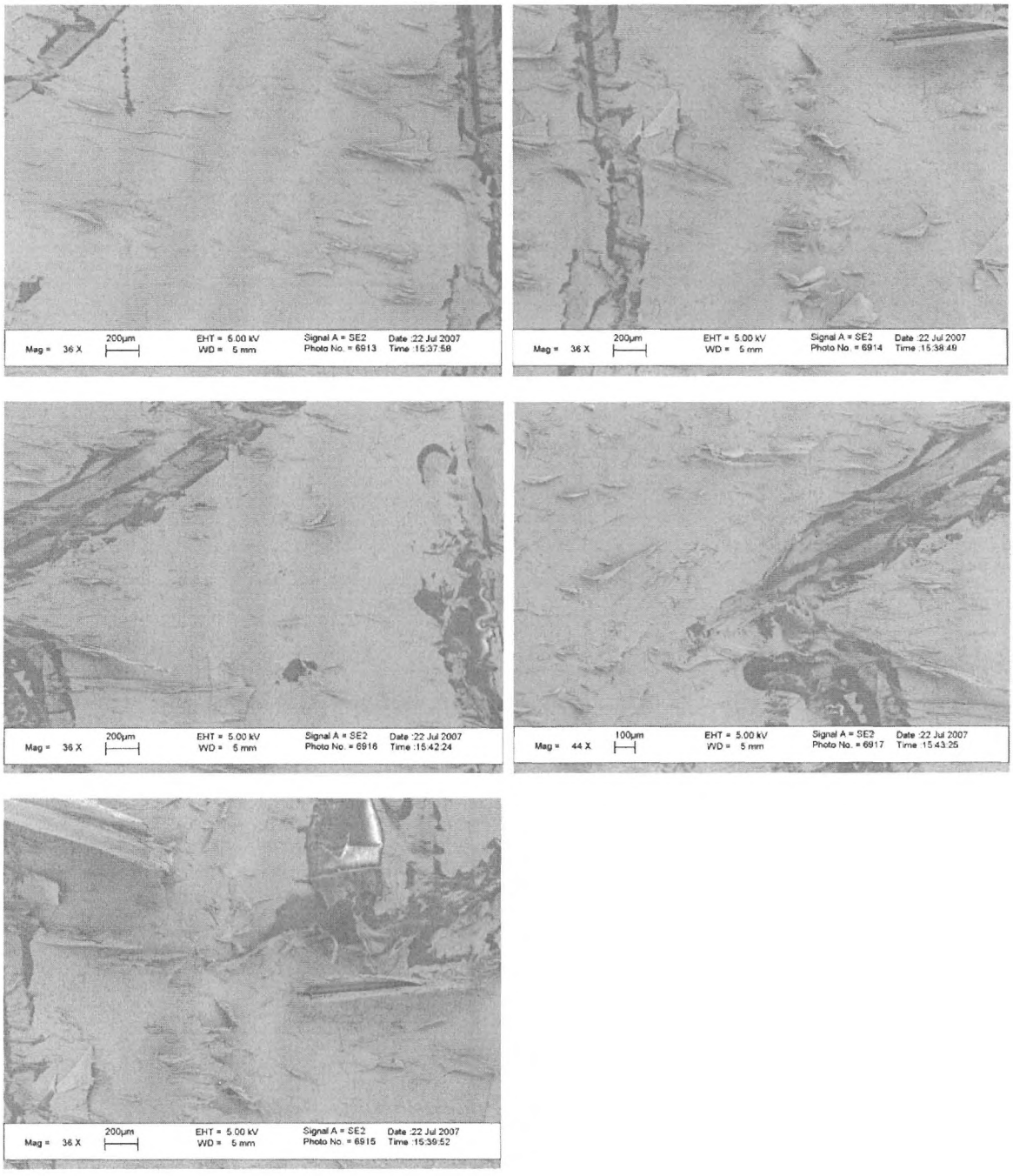
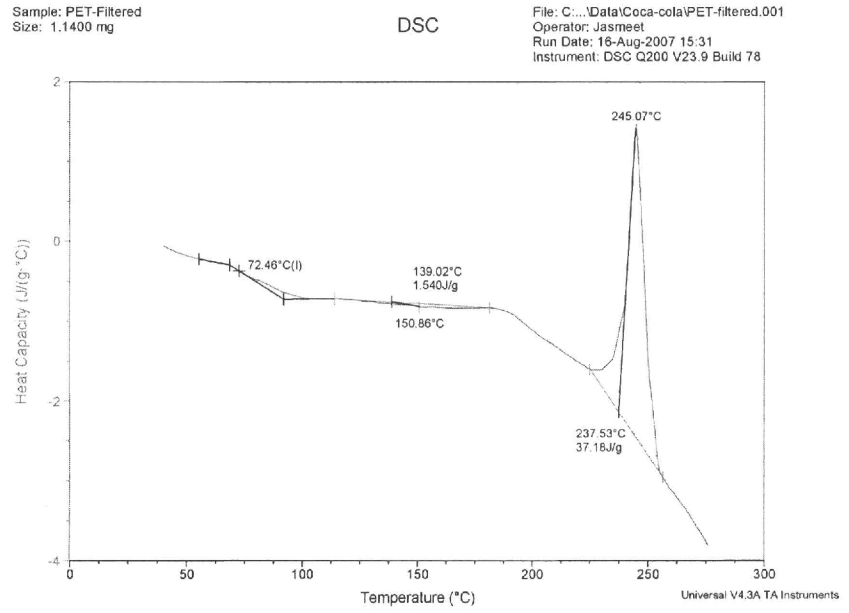


Figure 2. DSC of filtrate (upper plot) and undamaged PET (lower plot) – note this is only from one sample.



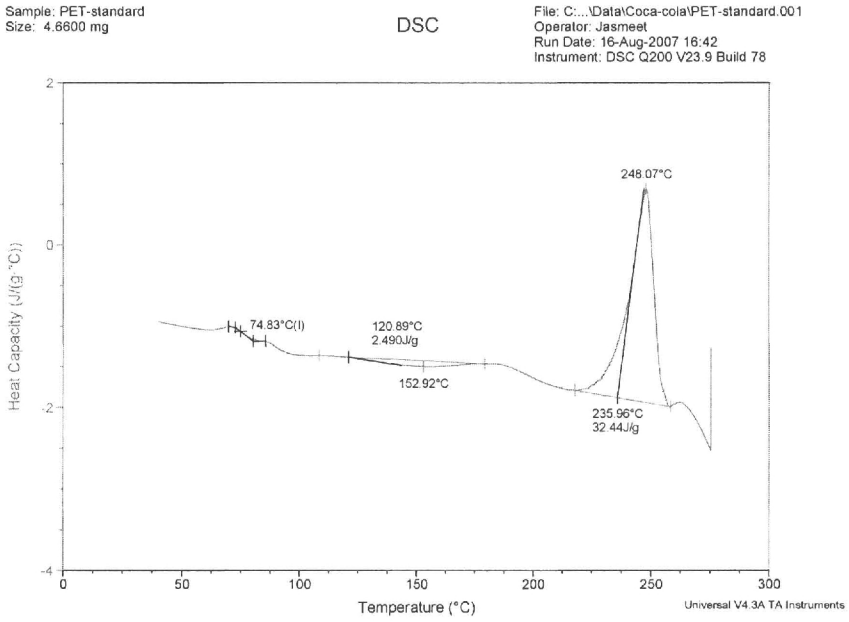
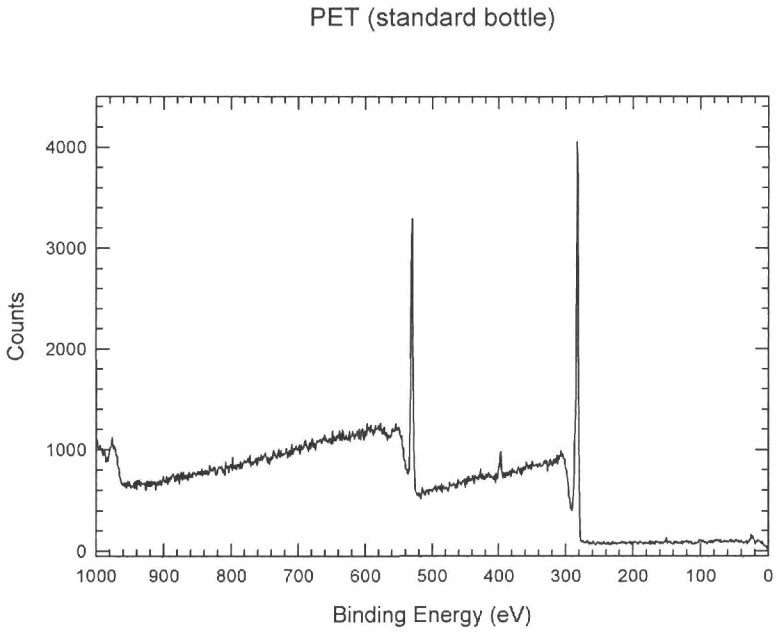
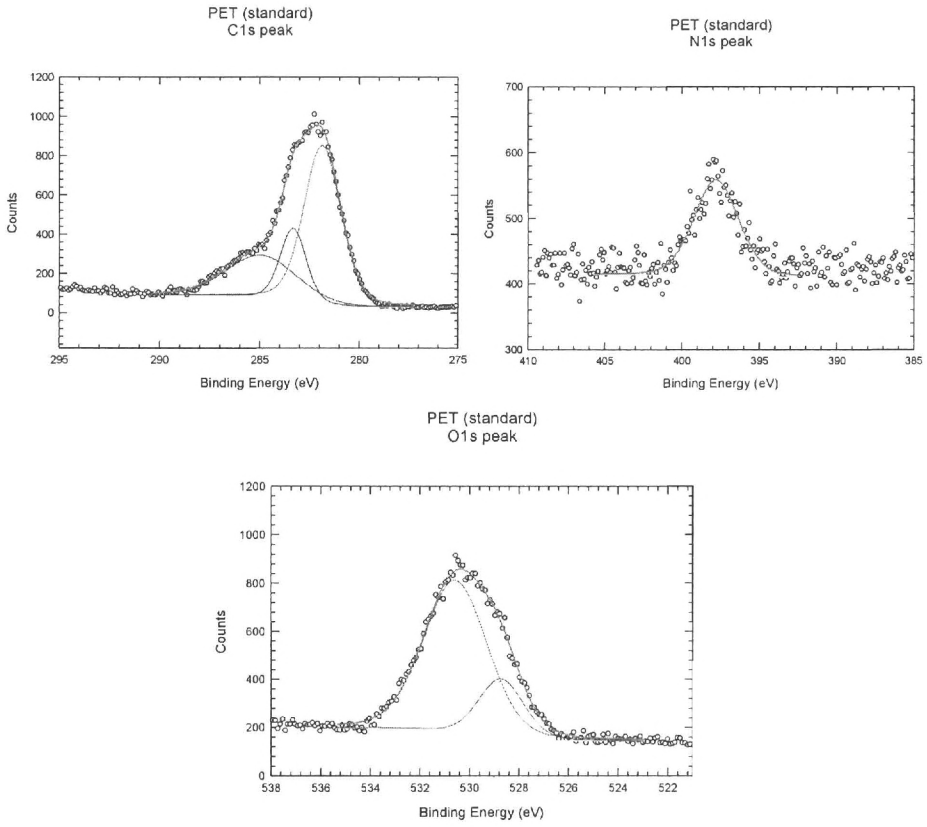



Figure 3. XPS data from internal surface of undamaged PET bottle.

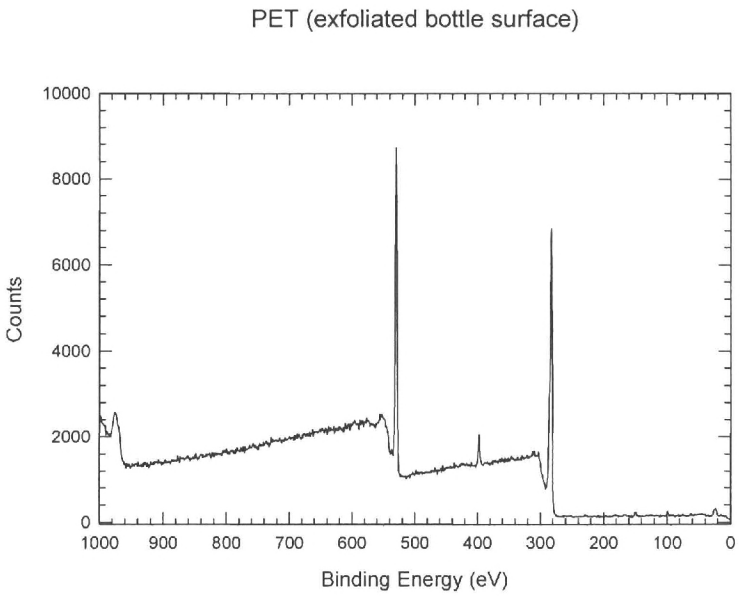
C1s peak at 282 eV, N1s at 397 eV and O1s at 530 eV.




high resolution XPS scans for C1s, N1s and O1s (as labeled), together with peak fits to the data:



Exfoliated surface:




high resolution XPS scans for C1s, N1s and O1s (as labeled), together with peak fits to the data: